INTRODUCTION

The corrosion of metals is a fundamental academic and industrial concern that has received a considerable amount of attention. Acid solutions are generally used for the removal of rust and scale in several industrial processes.¹

Organic inhibitors were applied extensively to protect metals from corrosion in many aggressive acidic media (e.g., in the acid pickling and cleaning processes of metals).²³ Organic compounds containing N, S and O atoms were found to be good corrosion inhibitors of metals particularly for active metals like Fe, Zn, Mg and Cu etc.⁴⁻¹² The effectiveness of these compounds as corrosion inhibitors has been interpreted in terms of their molecular structure, molecular size, and molecular mass, heteroatom present and adsorptive tendencies.¹³ Under certain conditions, the electronic structure of the organic inhibitors has a key influence on the corrosion inhibition efficiency to the metal. The inhibitors influence the kinetics of the electrochemical reactions which constitute the corrosion process and thereby modify the metal dissolution in acids. The existing data show that most organic inhibitors act by adsorption on the metal surface. Quite a number of studies have been carried out in determination of adsorptive of various compounds at the electrode/solution interface.¹⁴⁻¹⁶ A large number of organic compounds were studied as corrosion inhibitor, unfortunately most of the organic inhibitors used are very expensive and health hazards. Their toxic properties limit their field of application. Thus, it remains an important object to find cost-effective and non-hazardous inhibitors for the protection of metals against corrosion. In this connection, the influences of nontoxic organic compounds and drugs on the corrosion of metals in acid media were investigated by several authors.¹⁷⁻²⁵

The use of expired drugs as corrosion inhibitors can be traced back to 2009’s by R. S. Abdel Hameed, where expired ranitidine was used as corrosion inhibitors for Al in HCl corrosive medium.²⁶⁻²⁷ In 2011’s, R.S. Abdel Hameed, was reported the use of expired ranitidine drugs as non-toxic corrosion inhibitor for mild steel in hydrochloric acid medium.²⁸⁻²⁹

The objective of this work is to study the corrosion inhibitive action of phenytoin sodium for the corrosion of carbon steel in 1M HCl. The choice of this drug as a corrosion inhibitor is based on its environmentally friendly; its molecule has O, N atoms as active center atoms.

MATERIALS AND METHODS

Material

1- Phenytoin sodium
Chemical Composition of Carbon Steel Sample

The experiments were performed with C-steel alloy having the following chemical composition. The weight percentages of Si, Sn, Mo, Zn, Cu, Ni, Mn, Cr, V, Ti, Al, S, C and Fe of the C-steel alloy are 0.913, 0.019, 0.103, 0.02, 0.135, 0.242, 0.955, 1.09, 0.078, 0.073, 0.570, 0.389, 0.133 and 95.28 respectively.

Weight Loss Techniques

The test coupons were cut into 2 x 2 x 0.2 cm³. The samples were first mechanically polished with a fine grade emery paper in order to obtain a smooth surface, followed by degreasing in acetone then rinsed in distilled water and finally dried between two filter papers and weighed. All experimental were carried out at 25, 35, 45 and 55 ±1°C.

Electrochemical Techniques

Open Circuit Potential Measurements (OCP)

The open circuit potential also referred to as the equilibrium potential, the rest potential, or the corrosion potential (Ecorr) is the potential at which there is no current. The potential of the carbon steel electrodes immersed in the 1M HCl were measured (against a standard saturated calomel electrode, SCE, placed in the same compartment) as a function of immersion time in absence and presence of different concentrations from expired drugs.

Potentiodynamic Polarization

The electrical circuit used for determining the variation of electrode potential with the electrical current. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically with a scan rate 2 mV s⁻¹ from a low potential of -800 to -300 mV (SCE). Before each run, the working electrode was immersed in the test solution for 30 min to reach steady state. All potentials were measured against SCE. Measurements were obtained using a Voltalab 40 Potentiostat PGZ 301 combined with easy corrosion program (Voltamaster 4).

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance were obtained using a Voltalab 40 for all EIS measurements with a frequency range of 100 kHz to 50 mHz with a 4 mV sine wave as the excitation signal at open circuit potential. If the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis of a chart, we get a Nyquist Plot. The charge transfer resistance values (Rct) was calculated from the difference in impedance at lower and higher frequencies.

Scanning Electron Microscopy (SEM)

Joel (840 X Japan) scanning electron microscope was utilized to document the surface morphology of various specimens of carbon steel. In case of only polished surface and that immersed in 1 M HCl in absence and presence of an inhibitor. This instrument was operated in a secondary electron imaging made with an accelerating voltage of either 10 or 20Kev. Magnifications ranging from 50 to 10000X could be obtained by this tool in the present investigation three magnifications were selected 950, 1200 and 2400X.

RESULTS AND DISCUSSION

Weight Loss Measurements

Effect of Inhibitor Concentrations

Weight loss of C-steel in mg was calculated after fixed time 72 hours in absence and presence of different concentrations of expired drug. The data shows that, the values of weight loss increases with increasing time. The corrosion parameters such as weight loss (ΔW), rate of corrosion (k), surface coverage (θ) and inhibition efficiency (p) for Phenytoin sodium inhibitor are listed in Table (1).

The weight losses given by equation:

\[ \Delta W = (W_{1} - W_{2}) \]

Where, W₁ and W₂ are the weight of specimen before and after the reaction, respectively.

In all cases the increase of inhibitor concentrations was accompanied by a decrease in weight loss and an increase in the percentage inhibition. These results lead to conclusion that, the compounds under investigation are fairly efficient as inhibitors for C-steel dissolution in hydrochloric acid solution. To clear up the influence of this inhibitor on the mechanism of inhibition, the corrosion rate (k) was calculated using the following equation:

\[ k = (W_{\text{free}} - W_{\text{inh}}) / A \]

Where, k is the corrosion rate, W̃ and W_free are the weights loss of specimen in presence and absence of inhibitor respectively, A is the surface area in cm² and t is the time in hours.

The degree of surface coverage (θ) by the adsorbed molecules was calculated from equation [28]:

\[ \theta = (W_{\text{free}} - W_{\text{inh}}) / W_{\text{free}} \]

It was found that the degree of surface coverage (θ) of the inhibitor increases by increasing the inhibitor concentration. The inhibition efficiencies (P %) of expired drugs, were determined from equation:

\[ P\% = (\theta) \times 100 \]

Effect of temperature

The effect of rising temperature on both corrosion and corrosion inhibition of C-steel in 1M HCl solution at different temperatures was studied in range (25-55°C) and this investigated by weight loss measurements. The corrosion parameters such as weight loss (ΔW), rate of corrosion (k), surface coverage (θ) and inhibition efficiency (P %) for 500 ppm from Phenytoin sodium listed in Table (2). The data in table 2 illustrate that, the
Inhibition efficiency of the inhibitor decreases but increasing temperatures.

**Kinetic Parameters**

**Adsorption Isotherm**

The type of adsorption isotherm and the effect of temperature on the corrosion rate were studied. It is generally accepted that the studied expired drugs, compounds inhibit the corrosion process by adsorbing at the metal/solution interface.\(^{29}\)

In addition, it is believed that the formation of a solid organic molecule complex with the metal atom has received considerable attention.\(^{30}\)

The calculated values of the adsorption free energy, \(\Delta G_{ads}\), are given in Table 3.

- The equation that fits our results is that due to Langmuir isotherm and is given by the general equation:

\[
\frac{C}{\theta} = \frac{1}{K_{ads}} + \frac{C}{\theta} \quad (5)
\]

Where, \(K\) and \(C\) are the equilibrium constant of adsorption process and additive concentration, respectively.

The type of adsorption isotherm and the effect of temperature on the corrosion rate were studied. It is generally accepted that the studied expired drugs, compounds inhibit the corrosion process by adsorbing at the metal/solution interface.\(^{29}\)

In these cases, the plots of \(C/\theta\) versus \(C\) yield a straight line with intercept of \((1/ K_{ads})\) and with slope approximately equal unity were obtained. The small deviation from unity is generally attributed to the interaction of the adsorbed inhibitor molecules on heterogeneous carbon steel surface. This indicates that, the adsorption of inhibitor on the carbon steel surface in 1M HCl solution follows Langmuir’s adsorption isotherm. The free energy of adsorption (\(\Delta G_{ads}\)) at different temperatures was calculated from weight loss measurements by using equation (3).

\[
\Delta G_{ads} = RT \ln (55.5 K_{ads}) \quad (6)
\]

Where, \(C\) is the inhibitor concentration, \(\theta\) is the fraction of the surface covered, \(K_{ads}\) is the equilibrium constant of the inhibitor adsorption process, the value 55.5 is the molar concentration of water in solution in mol dm\(^{-3}\), \(R\) is the gas constant, \(T\) is the absolute temperature and \(\Delta G_{ads}\) is the standard free energy of adsorption.

The heat of adsorption (\(Q_{ads}\)), which is obtained from the slopes of the straight lines when \(K_{ads}\) plot versus \(1/T\), is equal to \(-Q_{ads}/R\). Since the pressure is a constant, \(Q_{ads}\) is equal to enthalpy of adsorption (\(\Delta H_{ads}\)) with good approximation. Entropy of inhibitor adsorption (\(\Delta S_{ads}\)) can be calculated using the following equation:

\[
\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \quad (7)
\]

The calculated values of the adsorption free energy, \(\Delta G_{ads}\), adsorption entropies, \(\Delta S_{ads}\), and adsorption enthalpies, \(\Delta H_{ads}\), are given in Table 3.

**Table 1:** Effect of PSD inhibitor concentration on carbon steel corrosion in 1M HCl at 25°C

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Conc., ppm</th>
<th>Weight loss, mg/cm(^2)</th>
<th>Corr. Rate, mg/cm(^2).hr</th>
<th>(\theta)</th>
<th>(P) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0</td>
<td>0.48</td>
<td>0.69444</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>PSD</td>
<td>100</td>
<td>0.1952</td>
<td>0.28241</td>
<td>0.593</td>
<td>59.3</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.1774</td>
<td>0.25666</td>
<td>0.6304</td>
<td>63.0</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.1357</td>
<td>0.19633</td>
<td>0.7173</td>
<td>71.7</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.1214</td>
<td>0.17564</td>
<td>0.7471</td>
<td>74.7</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.1001</td>
<td>0.1448</td>
<td>0.7915</td>
<td>79.1</td>
</tr>
</tbody>
</table>

**Table 2:** Effect of temperature on carbon steel corrosion in presence of 500 ppm of PSD inhibitor concentration in 1M HCl

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>Weight loss, mg/cm(^2)</th>
<th>Corr. Rate, mg/cm(^2).hr</th>
<th>(\theta)</th>
<th>(P) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.0391</td>
<td>0.1482</td>
<td>0.7915</td>
<td>79.1</td>
</tr>
<tr>
<td>35</td>
<td>0.0781</td>
<td>0.3389</td>
<td>0.7436</td>
<td>74.4</td>
</tr>
<tr>
<td>45</td>
<td>0.1674</td>
<td>0.72656</td>
<td>0.6892</td>
<td>68.9</td>
</tr>
<tr>
<td>55</td>
<td>0.3132</td>
<td>1.35938</td>
<td>0.6607</td>
<td>66.1</td>
</tr>
</tbody>
</table>

**Table 3:** Thermodynamic parameters of adsorption on carbon steel surface in 1M HCl containing different concentrations of PSD at different temperatures

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>(K_{ads}) x 10(^5)M(^{-1})</th>
<th>(\Delta G_{ads}) KJ mol(^{-1})</th>
<th>(\Delta H_{ads}) J mol(^{-1})</th>
<th>(\Delta S_{ads}) JK mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.2</td>
<td>-29.01</td>
<td>43.78</td>
<td>97.49</td>
</tr>
<tr>
<td>35</td>
<td>1.56</td>
<td>-29.11</td>
<td></td>
<td>94.65</td>
</tr>
<tr>
<td>45</td>
<td>1.16</td>
<td>-29.27</td>
<td></td>
<td>92.18</td>
</tr>
<tr>
<td>55</td>
<td>1.12</td>
<td>-30.09</td>
<td></td>
<td>91.87</td>
</tr>
</tbody>
</table>

**Electrochemical Studies**

**Potentiodynamic Polarization Techniques**

The extrapolation of anodic and/or cathodic Tafel lines of charge transfer controlled corrosion reaction gives the
corrosion current density, \( I_{\text{corr}} \) at corrosion potential, \( E_{\text{corr}} \). This method is based on the electrochemical theory of corrosion processes developed by Wagner and Traud.\(^{32}\)

The potential, \( E \), is plotted as a function of logarithm of current density (I) show the polarization curves for both anodic and cathodic reactions.

Figure (1) represent the potentiodynamic polarization plots for carbon steel electrode in 1M HCl in the absence and presence of different concentrations of the used inhibitor, at scanning rate 2mV/sec. The percentage inhibition efficiency \( P \) % is given by:

\[
P \% = \frac{(I_{\text{corr}} - I_{\text{corr(inh)}})}{I_{\text{corr}}}) \times 100 \quad \text{...... (8)}
\]

where, \( I_{\text{corr}} \) and \( I_{\text{corr(inh)}} \) are the corrosion current densities in absence and presence of inhibitors, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.

The degree of surface coverage (\( \theta \)) was calculated the following equation:

\[
\theta = \frac{(\beta_{\text{corr}} - \beta_{\text{corr(inh)}})}{\beta_{\text{corr}}} \quad \text{.................. (9)}
\]

Table (4) show the effect of inhibitor concentration on some electrochemical parameters, corrosion current density (\( I_{\text{corr}} \)), corrosion potential (\( E_{\text{corr}} \)), anodic and cathodic Tafel slopes (\( \beta_a \) and \( \beta_c \)), the degree of surface coverage (\( \theta \)) and the percentage of inhibition efficiency (\( P \) %) during the corrosion of C-steel electrode in 1M HCl solutions.

### Table 4: Potentiodynamic polarization parameters for corrosion of carbon steel in 1M HCl in absence and presence of different concentrations of PSD at 25°C at scanning rate 2mVs\(^{-1}\)

<table>
<thead>
<tr>
<th>Conc. of inhibitor</th>
<th>( E_{\text{corr}} ) mV</th>
<th>( I_{\text{corr}} ) mA cm(^{-2} )</th>
<th>( \beta_a ) mV dec(^{-1} )</th>
<th>( \beta_c ) mV dec(^{-1} )</th>
<th>( \theta )</th>
<th>( P ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-542.2</td>
<td>0.4622</td>
<td>154.9</td>
<td>-319.6</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>100</td>
<td>-566.8</td>
<td>0.1290</td>
<td>90.5</td>
<td>-128.6</td>
<td>0.7209</td>
<td>72.09</td>
</tr>
<tr>
<td>200</td>
<td>-573.2</td>
<td>0.1111</td>
<td>98.0</td>
<td>-127.2</td>
<td>0.7596</td>
<td>75.96</td>
</tr>
<tr>
<td>300</td>
<td>-568.8</td>
<td>0.0978</td>
<td>86.6</td>
<td>-121.9</td>
<td>0.7884</td>
<td>78.84</td>
</tr>
<tr>
<td>400</td>
<td>-577.1</td>
<td>0.0858</td>
<td>97.3</td>
<td>-119.6</td>
<td>0.8143</td>
<td>81.43</td>
</tr>
<tr>
<td>500</td>
<td>-577.6</td>
<td>0.0842</td>
<td>93.8</td>
<td>-116.0</td>
<td>0.8178</td>
<td>81.78</td>
</tr>
</tbody>
</table>

### Electrochemical Impedance Spectroscopy (EIS)

The corrosion behavior of C-steel in 1M HCl solution in the absence and presence of the studied inhibitor was investigated by EIS method at 25°C. Figure (2) show the Nyquist plots for carbon steel in 1M HCl solution in the absence and presence of different concentrations of inhibitor at 25°C. The Nyquist plots were regarded as one part of a semicircle. The impedance diagram shows the same trend (one capacitive loop); however, the diameter of this capacitive loop increases with increasing concentration.

The presence of the inhibitor increases the impedance but does not change other aspects of the behavior. These results support the results of polarization measurements that the inhibitor does not alter the electrochemical reactions responsible for corrosion. It inhibits corrosion primarily through its adsorption on the metal surface.\(^{33, 34}\)

The charge transfer resistance values (\( R_{\text{ct}} \)) are calculated from the difference in impedance at lower and higher frequencies, as suggested by Haruyama and Tsuru.\(^{26}\) To obtain the double-layer capacitance (\( C_d \)), the frequency at which the imaginary component of the impedance at maximum \( f (-Z''_{\text{im}}) \) is found and \( C_d \) values are calculated from the following equation: \(^{32}\)

\[
f (-Z''_{\text{im}}) = 1/(2\pi f C_d R_{\text{ct}}) \quad \text{................. (10)}
\]

The impedance quantitative results can be seen in Tables (5). It is clear that, the corrosion of steel is obviously inhibited in the presence of the inhibitor. It is apparent that, the impedance response for carbon steel in 1M HCl changes significantly with increasing inhibitor concentration.

In the case of the electrochemical impedance spectroscopy, the inhibition efficiency is calculated using charge transfer resistance as follow:

\[
P \% = \frac{(R_{\text{ct}} - R_{\text{ct(inh)}})}{R_{\text{ct}}} \times 100 \quad \text{................. (11)}
\]

Where, \( R_{\text{ct}} \) and \( R_{\text{ct(inh)}} \) are the charge transfer resistance values in the absence and presence of inhibitor for C steel in 1M HCl, respectively.

![Figure 1: Potentiodynamic polarization curves for the carbon steel in 1M HCl in the absence and presence of different concentrations of PSD at scanning rate 2 mV s\(^{-1}\)](image_url)

As the inhibitor concentration increased, the \( R_{\text{ct}} \) values increased, but the \( C_d \) values tended to decrease. The
decrease in $C_{dl}$ value is due to the adsorption of inhibitor on the metal surface.\textsuperscript{36} The inhibition efficiency increases with increasing inhibitor concentration. This fact suggests that the inhibitor molecules may first be adsorbed on the steel surface and cover some sites of the electrode surface. These layers protect steel surface.

Table 5: EIS parameters for corrosion of carbon steel in 1M HCl in the absence and presence of different concentrations of PSD at 25°C

<table>
<thead>
<tr>
<th>Conc. of inhibitor</th>
<th>$R_\text{ct}$ Ohm cm$^2$</th>
<th>$R_s$ Ohm cm$^2$</th>
<th>$C_{dl}$ µF cm$^{-2}$</th>
<th>$\theta$</th>
<th>P%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>104.269</td>
<td>2.18</td>
<td>40.95</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>100</td>
<td>245.329</td>
<td>2.95</td>
<td>7.49</td>
<td>0.5749</td>
<td>57.49</td>
</tr>
<tr>
<td>200</td>
<td>281.354</td>
<td>2.63</td>
<td>6.15</td>
<td>0.6294</td>
<td>62.94</td>
</tr>
<tr>
<td>300</td>
<td>368.806</td>
<td>2.62</td>
<td>3.35</td>
<td>0.7172</td>
<td>71.72</td>
</tr>
<tr>
<td>400</td>
<td>440.969</td>
<td>1.59</td>
<td>2.42</td>
<td>0.7635</td>
<td>76.35</td>
</tr>
<tr>
<td>500</td>
<td>496.703</td>
<td>1.51</td>
<td>1.98</td>
<td>0.7900</td>
<td>79.0</td>
</tr>
</tbody>
</table>

Figure 2: Nyquist plots for the carbon steel in 1M HCl in the absence and presence of different concentrations of PSD

Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high energy beam of electrons in a raster scan pattern. The electrons interact with the atoms (at or near the surface of the sample) that make up the sample producing signals that contain information about the sample’s surface topography.

Figure 3a: Scanning electron micrographs of carbon steel sample after polishing

Figure 3b: Scanning electron micrographs of carbon steel sample after immersion in 1M HCl solution without inhibitor

Figure 3c: Scanning electron micrographs of carbon steel sample after immersion in 1M HCl solution containing 500 ppm of PSD

CONCLUSION

Based on the obtained results, the following conclusions are accomplished:-

- The used expired drug is excellent inhibitor and act as the mixed type inhibitors for carbon steel corrosion in hydrochloric acid solution.
- Inhibition efficiencies increased by increasing inhibitor concentration and temperatures up to 328 K.
- The uniform increasing inhibition efficiency as the function of concentration and the adsorption of the additive obeys the Langmuir adsorption isotherm. The adsorption of the inhibitor on carbon steel is a physicosorption type.
- Thermodynamic parameters of the adsorption ($E^*$, $\Delta H^*$ and $\Delta S^*$) were calculated and showed that the used inhibitor decreased the rate of corrosion.
REFERENCES


26. Abd Hameed RS, Expired drugs as corrosion inhibitors for metals and alloys, journal of physical chemistry, PCAA, 8(4), 2013, 146-149.


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